IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant	:	Arthur Sherman
App. No	:	10/683,727
Filed	:	October 10, 2003
For	:	SEQUENTIAL CHEMICAL VAPOR DEPOSITION
Examiner	:	Gambetta, Kelly M.
Art Unit	:	1792
Conf No.	:	1627

DECLARATION OF SUVI HAUKKA UNDER 37 C.F.R. § 1.132

Mail Stop AF
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

I, Suvi Haukka, do hereby declare and say as follows:

1. I am currently employed as an Executive Scientist for ALD applications for ASM Microchemistry Oy, in Helsinki, Finland. For the past nineteen years I have worked in various capacities including Research Scientist, Catalyst Technology Manager, Process Development Manager and R&D Manager which all have been related to atomic layer deposition (ALD). In particular, my work has focused on ALD and applications of it for semiconductor equipment, processes, and devices as well as development of ALD apparatus. Over the course of my career, I have been an author on over 60 scientific papers, primarily concerning ALD processes, applications and apparatus. In addition, I am an inventor of more than 60 patents and patent applications in the field of semiconductor fabrication. In 1994 I earned a Doctor of Philosophy degree from Laboratory of Analytical Chemistry, University of Helsinki, Finland.

2. I have read and understand the claims in the present patent application, application serial number 10/683,727. I understand that the claims concern a process of growing a thin film of Al_2O_3 on a substrate (Claim 1).

3. I have read and understand the rejections in the Office Action dated July 31, 2009. I understand that the Examiner has asserted that the above described claims (Claims 1-5) are obvious in light of a combination of "Surface chemistry of Al_2O_3 deposition using $Al(CH_3)_3$ and H_2O in a binary reaction sequence" (Dillon) in view of Penneck et al. (U.S. Pat. No. 4,985,313).

4. The Examiner has asserted that the aluminum oxide layer thickness in Dillon is a result-effective variable that can be modified by routine experimentation. The Examiner also has asserted that it would have been obvious to a person having ordinary skill in the art at the time the invention was made to form more than one monolayer of Al_2O_3 per cycle, since it has been held that discovering an optimum value of a result-effective variable involves only routine skill in the art.

5. After having read Dillon it is my opinion that the ordinary engineer would not be able to modify the ALD process of Dillon through routine experimentation to deposit more than a monolayer of aluminum oxide per cycle.

6. ALD type processes are based on controlled, self-limiting surface reactions of precursor chemicals. Gas phase reactions are avoided by feeding the precursors alternately and sequentially into the reaction chamber. Vapor phase reactants are separated from each other in the reaction chamber, for example, by removing excess reactants and/or reactant byproducts from the reaction chamber between reactant pulses. For example, reactant separation are done in Dillon by evacuating reaction chamber to pressure of $(5\text{-}6) \times 10^{-5}$ torr in such way that no physisorbed water are present (page 232).

7. In ALD processes the deposition temperatures are maintained below the thermal decomposition temperature of the reactants but at a high enough level to avoid condensation of reactants and to provide the activation energy for the desired surface reactions. Surface saturation ensures reactant occupation of all available reactive sites (subject, for example, to physical size or "steric hindrance" restraints) and thus ensures excellent step coverage.

8. I would not expect to be able to modify the ALD process of Dillon to deposit more than one monolayer of aluminum oxide per cycle. Within the ALD temperature window

(below the decomposition temperature of the reactants and above the minimum temperature required for chemisorption of the reactants), the chemisorption of the reactants is self limiting, and limited to less than a monolayer of material. ALD would not work at temperatures below the temperature required for the activation energy of the desired surface reactions.

9. Increasing the temperature above the decomposition temperature of one of the reactants would undesirably disrupt the self-limiting nature of the ALD process and adversely affect the ability of the process to deposit conformal thin layers.

10. Supplying a greater amount of TMA or water would not increase the deposition of aluminum oxide to above one monolayer per cycle in Dillon's ALD process. The chemisorption of TMA and water is self-limiting because after reactants chemisorb to the available surface sites there are no more available sites for chemisorption. Thus, providing additional reactants in the process of Dillon will not increase the deposition of aluminum oxide to above one monolayer per cycle as also stated by Dillon that earlier work has indicated a growth rate of 0.33 monolayers of Al_2O_3 per reaction cycle under similar conditions (page 241).

11. I am not aware of any process variables, such as reactor pressure, which could be used to modify the ALD process of Dillon to achieve a deposition rate above one monolayer per cycle.

12. I am not aware of any prior art that discloses formation of greater than one monolayer of aluminum oxide using an ALD process with TMA and water as reactants.

13. I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true. I declare that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Respectfully submitted,

Dated: September 28, 2009 By: _____

Suvi Haukka

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CURRICULUM VITAE

(29.09.2009)

Personal information

Name	Suvi Päivikki Haukka (os. Ojala)
Date of birth	March 4, 1959
Place of birth	Hämeenkoski, Finland
Family relations	Married to Jarmo Haukka from 1986, two boys: Aleksis born in 1988 and Elias in 1995
Address	Kymintie 28, 00560 Helsinki
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Education

Doctor of Philosophy	University of Helsinki, Laboratory of Analytical Chemistry, 1994
Master of Science	University of Helsinki, Laboratory of Radiochemistry, 1987
Secondary school graduate	High School in Orivesi, Finland 1979
High School	John F. Kennedy High School, Cedar Rapids, Iowa, USA, 1978

Professional Career

Executive Scientist	ASM Microchemistry Oy	22.11.2001 –
R&D Manager	ASM Microchemistry Oy	1.1.2001 – 22.11.2001
Process Development Manager	ASM Microchemistry Oy	1.1.1998 – 31.12.2000
Catalyst Technology Manager	Microchemistry Oy	1.1.1996 – 31.12.1997
Research Scientist	Microchemistry Oy	1.1.1994 – 31.12.1995
Research Scientist	Academy of Finland/ Microchemistry Oy	1.4.1990 – 31.12.1993
Research Scientist	University of Helsinki	1.1.1989 – 31.3.1990
Research Scientist	University of Helsinki	1.7.1987 – 31.12.1987
Ass. Research Scientist	Radiation and Nuclear Safety Authority	28.5.1986 – 31.12.1986
Research assistant	Radiation and Nuclear Safety Authority	16.9.1985 – 31.12.1985
Research assistant	Radiation and Nuclear Safety Authority	25.6.1984 – 31.12.1984
Research assistant	VTT Technical research Center of Finland	1.1.1984 – 1.6.1984
Research assistant	Radiation and Nuclear Safety Authority	1.7.1983 – 15.9.1983

Short biography of Dr. Suvi Haukka of ASM Microchemistry

Dr. Suvi Haukka is currently working as Executive Scientist for ALD applications at ASM Microchemistry which is a research company owned by ASM International, a global company that together with its subsidiaries designs and manufactures equipment and materials used to produce semiconductor devices. In 1990 Suvi Haukka joined Microchemistry to carry out her PhD studies on the atomic layer by atomic layer growth. After completing her PhD in 1993 she worked at Microchemistry first as Research Scientist and later as Department Manager. At ASM Microchemistry after ASM International acquired Microchemistry in 1999 she was first responsible for the atomic layer deposition (ALD) process development and later for the ALD technology development until the end of 2001. Dr. Haukka has authored and co-authored over 60 technical publications, is inventor of more than 60 patents (about 30 issued US patents) and other pending applications related to ALD. Dr. Haukka holds an MSc and PhD in Chemistry from the University of Helsinki (Finland).

Publications, presentations and patents

Publications

1. Pamela Fischer, Dieter Pierreux, Olivier Rouault, Jacky Sirugue, Peter Zagwijn, Eva Tois, and Suvi Haukka, ***Batch Atomic Layer Deposition of HfO_2 and ZrO_2 Films Using Cyclopentadienyl Precursors***, Fall 08, ECS transactions, 2008, submitted, paper presented in the ECS Conference in Honolulu in 2008.
2. W.-M. Li, R. Huggare, E. Tois, R. Matero, S. Haukka, and M. Tuominen, ***ALD of metal nitrides and carbides,*** Extended abstract prepared by S. Haukka for the EuroCVD conference held in Den Haag, The Netherlands, in September 2007.
3. Fedorenko Y., Swerts J., Maes J. W., Tois E., Haukka S., Wang C.-G., Wilk G., Delabie A., Denweerd W., De Gendt, S., ***Atomic layer deposition of hafnium silicate from $HfCl_4$, $SiCl_4$ and H_2O***, Electrochem. Solid-State Lett. 10 (2007) H149-H152.
4. Haukka S., ***ALD technology – present and future challenges,*** ECS Transactions – Cancun 2006" Volume 3, "Atomic Layer Deposition Applications 2"
5. Elers, K.-E.; Blomberg, T.; Peussa, M.; Aitchison, B.; Haukka, S.; Marcus, S. ***Film uniformity in atomic layer deposition,*** Chemical Vapor Deposition (2006), 12(1), 13-24.
6. Matero, R.; Rahtu, A.; Haukka, S.; Tuominen, M.; Vehkamäki, M.; Hatanpää, T.; Ritala M.; Leskelä, M.; ***Scale-up of the barium titanate atomic layer deposition process onto 200mm wafer,*** Poster and paper presented in the 208th ECS Meeting in Los Angeles, California, in October 16-21, 2005.
7. H. Huotari, S. Haukka, R. Matero, E. Tois, A. Rahtu and M. Tuominen, ***Atomic Layer Deposition of niobium nitride and niobium silicon nitride thin films for metal electrodes,*** Poster and paper presented in the 208th ECS Meeting in Los Angeles, California, in October 16-21, 2005.
8. Soininen, P. J.; Elers, K.-E.; Saanila, V.; Kaipio, S.; Sajavaara, T.; Haukka, S., ***Reduction of copper oxide film to elemental copper,*** Journal of the Electrochemical Society (2005), 152(2), G122-G125.
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10. Kim, Soo-Hyun; Oh, Su Suk; Kim, Hyun-Mi; Kang, Dae-Hwan; Kim, Ki-Bum; Li, Wei-Min; Haukka, Suvi; Tuominen, Marko. ***Characterization of atomic-layer-deposited WN_xC_y thin film as a diffusion barrier for copper metalization.*** Journal of the Electrochemical Society (2004), 151(4), C272-C282.
11. Haukka, Suvi; Tuominen, Marko; Vainonen-ahlgren, Elizaveta; Tois, Eva; Li, Wei-min; Maes, Jan Willem. ***Effect of starting surface in atomic layer deposition.*** Proceedings - Electrochemical Society (2003), 2003-14(Advanced Short-Time Thermal Processing for Si-Based CMOS Devices), 405-416.
12. Rittersma, Z. M.; Massoubre, D.; Roozeboom, F.; Verheijen, M. A.; van Berkum, J. G. M.; Tamminga, Y.; Dao, T.; Snijders, J. H. M.; Vainonen-ahlgren, E.; Tois, E.; Tuominen, M.; Haukka, S. ***Rapid thermal annealing of atomic layer deposited hafnium-silicate/poly-silicon layers.*** Proceedings - Electrochemical Society (2003), 2003-14(Advanced Short-Time Thermal Processing for Si-Based CMOS Devices), 273-280.

13. Kim, Soo-hyun; Oh, Su Suk; Kim, Hyun-mi; Kang, Dae-hwan; Kim, Ki-bum; Li, Wei-min; Haukka, Suvi; Tuominen, Marko. ***Characterization of atomic layer deposited WN_xC_y thin film as a diffusion barrier for copper metallization.*** School of Materials Science and Engineering, Materials Research Society Symposium Proceedings (2003), 766 (Materials, Technology and Reliability for Advanced Interconnects and Low-k Dielectrics--2003), 445-451.
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15. Li, Wei-Min; Tuominen, Marko; Haukka, Suvi; Sprey, Hessel; Raaijmakers, Ivo J. ***Diffusion barrier material for Cu metallization using ALD-WN_xC_y.*** Solid State Technology (2003), 46(7), 103-104, 106.
16. Kim, Soo-Hyun; Oh, Su Suk; Kim, Ki-Bum; Kang, Dae-Hwan; Li, Wei-Min; Haukka, Suvi; Tuominen, Marko. ***Atomic-layer-deposited WN_xC_y thin films as diffusion barrier for copper metallization.*** Applied Physics Letters (2003), 82(25), 4486-4488.
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18. Elers, K.-E.; Saanila, V.; Li, W.-M.; Soininen, P. J.; Kostamo, J. T.; Haukka, S.; Juhanoja, J.; Besling, W. F. A. ***Atomic layer deposition of WxN/TiN and WNxCy/TiN nanolaminates.*** Thin Solid Films (2003), 434(1-2), 94-99.
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20. Vainonen-Ahlgren, E.; Tois, E.; Ahlgren, T.; Khriachtchev, L.; Marles, J.; Haukka, S.; Tuominen, M. ***Atomic layer deposition of hafnium and zirconium silicate thin films.*** Computational Materials Science (2003), 27(1-2), 65-69.
21. Haukka S.; Raaijmakers. ***Advanced liners for metallization.*** Semicon Europe, Technical Symposium, Germany, Munich, April 17, 2002.
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Oral presentations

1. S. Haukka, ***ALD Fundamentals, ALD Precursors, Equipment and Manufacturing,*** tutorial presentation in the ALD2009 workshop, July 19, 2009, Monterey
2. Eva Tois, Suvi Haukka, Marko Tuominen, K.B. Jinesh, Riccardo Forti, Yann Lamy, Wim Besling and Fred Roozeboom, ***Atomic Layer Deposition of Erbium-Doped HfO_2 Films,*** oral presentation in the ALD2009 conference in Monterey in July 22, 2009
3. S. Haukka, **ALD from Basic Research to High Volume Manufacturing,** Baltic ALD Conference, June 15-16, Uppsala Sweden (invited talk)
4. S. Haukka, E. Tois, D. Pierreux, P. Fischer, G. Dilliway, and P.M. Zagwijn, ***Comparison of the Behavior of Zirconium Cyclopentadienyl Precursors in ALD Reactors with Varying Substrate Surface Area,*** ALD2008 conference in Bruges, Belgium, june 29 – July 2, 2008 (oral presentation)
5. W.-M. Li, R. Huggare, E. Tois, R. Matero, S. Haukka, and M. Tuominen, ***ALD of metal nitrides and carbides,*** EuroCVD conference held in Den Haag, The Netherlands, in September 2007. (Invited talk)
6. Haukka S., ***MONA – merging optics and nanotechnologies: the nanophotonics technology roadmap,*** NTNE (Nanotechnology Northern Europe) 2007, Congress and Exhibition 27-29 March 2007, Helsinki, Finland. (Oral presentation, presented on the behalf of the MONA EU project consortium)
7. Haukka S., ***Ohutkalvo - nanoteknologinen innovaatio laboratoriosta tuotantoon,*** Helsingin yliopiston viestintäosaston järjestämässä tiedotusvälineiden edustajille muutaman kerran vuodessa tutkimusta taustoittavia "Tästä puhutaan – tilaisuudessa", 21.3.2007.
8. Haukka, S., ***ALD Technology – present and future challenges***, The 210th ECS (Electrochemical Society) Meeting, October 29 – November 3, 2006, in Cancun, Mexico. (Invited talk, in Atomic Layer Deposition Applications 2 – session.)
9. Haukka, S., ***Overview of reaction mechanisms related to ALD growth***, ALD 2006, AVS Topical Conference, in Korea, Seoul, July 24-26, 2006. (Invited talk).

10. Haukka, S., ***The future challenges and opportunities of atomic layer deposition: In the workshop on Challenges of the new materials in semiconductor manufacturing,*** Semicon® Europe, Germany, Munich, April 5, 2006. (Invited talk)
11. Haukka, S., Verghese, M.; Shero, E.; Pierreux, D.; Leskelä, M.; Ritala, M.; Hatanpää, T., ***What a Successful Atomic Layer Deposition Process Requires from Precursors? In the workshop on precursos,*** Semicon® Europe, Germany, Munich, April 6, 2006. (Invited talk)
12. Haukka, S., ***The future challenges and opportunities of ALD technology***: In the ALD seminar in Eindhoven, The Netherlands on March 31, 2006. (Invited talk).
13. Haukka S., ***Experimental Study of ALD Growth Mechanisms (with examples on rare earth oxides),*** ESF/PESC Exploratory Workshop: Rare Earth Oxide Thin Films: growth, characterization, and applications, San Remo, Italy, 11-13 May 2005. (Invited talk).
14. Haukka S., Tuominen M., ***Limiting of Incubation time in ALD growth of Ru***, ALD 2005, AVS Topical Conference, in USA, San Jose, August 8-10, 2005.
15. Kostamo J., Haukka S., ***ALD surface reactions of Cu precursors***, ALD 2004, AVS Topical Conference, in Finland, Helsinki, August 16-18, 2004.
16. Haukka S. ***Influence of precursor characteristics on ALD thin film growth***, NEMat (Nano-Electronic Materials) Conference 2004, in France, Grenoble, March 2-4, 2004. (Invited talk).
17. Haukka S. Short course lecture: ***Importance of starting surface in ALD***, Advanced Metallization Conference (AMC) 2003, in Canada, Montreal, October 21-23, 2003. (Invited talk).
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19. Haukka S. Short course lecture: ***ALD in metallization***, IEEE International Interconnect Technology Conference, 6th, Burlingame, CA, USA, June 1, 2003. (Invited talk).
20. Haukka, Suvi; Tuominen, Marko; Vainonen-ahlgren, Elizaveta; Tois, Eva; Li, Wei-min; Maes, Jan Willem. ***Effect of starting surface in atomic layer deposition.*** Proceedings - Electrochemical Society (2003), 2003-14(Advanced Short-Time Thermal Processing for Si-Based CMOS Devices), 405-416. (Invited talk)
21. Smith S., Book G., Li W.-M., Sun Y., Gillespie P., Tuominen M., Pfeifer K., Haukka S. ***The application of ALD WN_xC_y as a copper diffusion barrier,*** IEEE International Interconnect Technology Conference, 6th, Burlingame, CA, USA, June 1, 2003. (I gave the oral presentation for S. Smith).
22. Haukka S. Characteristics features of atomic layer-by-layer growth, The 4th International Symposium on Control of Semiconductor Interfaces (ISCSI-4), Karuizawa, Japan, October 21-25, 2002. (Invited talk).
23. Blin D., Haukka S., Viitanen M., Damlencourt J.-F., Holliger P. Martin F. ***Study of the initial steps of ALD HfO_2 growth on SiO_2.*** ALD 2002, AVS Topical Conference, in Korea, Seoul, August 19-21, 2002. (I gave the talk for D. Blin)
24. Haukka, Suvi; Raaijmakers, Ivo; Elers, Kai-Erik; Kostamo, Juhana; Li, Wei-Min; Sprey, Hessel; Soininen, Pekka J.; Tuominen, Marko. ***Deposition of Cu barrier and seed layers with atomic layer control.*** Proceedings of the IEEE International Interconnect Technology Conference, 5th, Burlingame, CA, United States, June 3-5, 2002 (2002), 279-281. (Invited talk)
25. Haukka S.; Raaijmakers. ***Advanced liners for metallization.*** Semicon Europe, Technical Symposium, Germany, Munich, April 17, 2002. (Invited talk)
26. Haukka, Suvi; Elers, Kai-Erik; Tuominen, Marko. ***Atomic layer CVD for continuously shrinking devices.*** Materials Research Society Symposium Proceedings (2001), 612(Materials, Technology and Reliability for Advanced Interconnects and Low-k Dielectrics), D6.4/1-D6.4/6. (Invited talk) **MRS Spring meeting 2001**
27. Haukka S. ALD processes and equipment. ALD 2004, AVS Topical Conference, in USA, Monterey, August 19-21, 2001. (Invited talk).
28. Haukka S.; Tuominen M.; Granneman E. ***Atomic layer chemical vapor deposition of high-k gate dielectrics.*** Presented in high-k dielectrics session organized by Semieducation on the 5th of April, 2000 in Munchen. (Invited talk)
29. Haukka S.; Tuominen M.; Kanniainen T. ***Atomic layer chemical vapor deposition – an advanced method for the deposition of high quality thin films***, extended abstract in the 29th IUVSTA workshop on selective and functional deposition technologies as applied to ULSI technology, November 19-24, 2000, Mie, Japan. (Invited talk).
30. Haukka, Suvi; Lindblad, Marina; Suntola, Tuomo. ***Growth mechanisms of mixed oxides on alumina.*** Applied Surface Science (1997), 112, 23-29. (oral presentation in ALD conference, Linz, Austria, 1996)
31. Haukka, S.; Lakomaa, E.-L.; Suntola, T. ***Analytical and chemical techniques in the study of surface species in atomic layer epitaxy.*** Thin Solid Films (1993), 225(1-2), 280-3. (oral presentation in ALD conference, Raleigh, North Carolina, USA, 1992)
32. + A number of presentations in various semiconductor companies in USA, Europe, Japan. Korea and Taiwan
33. + A number of presentations related to ALD catalyst applications

34. + A number poster presentations

Patents

1. **US 7,102,235:** Conformal lining layers for damascene metallization
2. **US 7,045,406:** Method of forming an electrode with adjusted work function
3. **US 7,038,284:** Methods for making a dielectric stack in an integrated circuit
4. **US 6,933,225:** Graded thin films
5. **US 6,902,763:** Method of depositing nanolaminate thin films on sensitive surfaces
6. **US 6,887,795:** Method of growing electrical conductors
7. **US 6,863,727:** Method of depositing transition metal nitride thin films
8. **US 6,858,524:** Method of depositing barrier layer for metal gates.
9. **US 6,852,635**: Method for bottomless deposition of barrier layers in integrated circuit metallization schemes.
10. **US 6,831,315:** Conformal thin films over textured capacitor electrodes.
11. **US 6,806,145**: Low temperature method of forming a gate stack with high k layer deposited over an interfacial oxide layer.
12. **US 6,800,552:** Deposition of transition metal carbides.
13. **US 6,794,314:** Method of forming ultra thin oxide layer.
14. **US 6,780,704:** Conformal thin films over textured capacitor electrodes.
15. **US 6,759,325:** Sealing porous structures.
16. **US 6,727,169:** Method of making conformal lining layers for damascene metallization.
17. **US 6,703,708:** Graded thin films.
18. **US 6,699,783:** Method of controlling conformality with alternating layer deposition.
19. **US 6,686,271:** Protective layers prior to alternating layer deposition.
20. **US 6,664,192:** Method for bottomless deposition of barrier layers in integrated circuit metallization schemes.
21. **US 6,660,660:** Methods of making a dielectric stack in an integrated circuit.
22. **US 6,534,395:** Method of forming graded thin films using alternating pulses of vapor phase reactants.
23. **US 6,500,780:** Method of preparing heterogeneous catalysts of desired metal content.
24. **US 6,492,283:** Method of forming ultra thin oxide layer.
25. **US 6,482,740:** Method of growing electrical conductors by reducing metal oxide film with organic compound containing –OH, -CHO, or -COOH.
26. **US 6,482,733,** Protective layers prior to alternating layer deposition.
27. **US 6,482,262:** Deposition of transition metal carbides.
28. **US 6,391,785:** Method for bottomless deposition of barrier layers in integrated circuit metallization schemes.

+ 33 US patent applications (including CIP etc.)